

CLAIMS

1. A process for producing a vinyl-cis-polybutadiene rubber, which comprises mixing (A) vinyl-cis-polybutadiene obtained by (1) a step of adding a cis-1,4-polymerization catalyst obtainable from an organoaluminum compound and a soluble cobalt compound to a mixture containing 1,3-butadiene and a hydrocarbon-based organic solvent as the major components and having an adjusted water content, thereby subjecting the 1,3-butadiene to cis-1,4-polymerization and subsequently, (2) a step of making a catalyst obtainable from a soluble cobalt compound, an organoaluminum compound represented by the general formula,  $AlR_3$  (wherein R represents an alkyl group having from 1 to 6 carbon atoms, a phenyl group, or a cycloalkyl group), and carbon disulfide present in the resulting polymerization reaction mixture, thereby subjecting the 1,3-butadiene to 1,2-polymerization; and (B) cis-polybutadiene obtained by a step of adding said cis-1,4-polymerization catalyst, thereby subjecting the 1,3-butadiene to cis-1,4-polymerization.
2. A process for producing a vinyl-cis-polybutadiene rubber, which comprises mixing (A) a vinyl-cis-polybutadiene solution obtained by (1) a step of adding a cis-1,4-polymerization catalyst obtainable from an organoaluminum compound and a soluble cobalt compound to a mixture containing 1,3-butadiene and a hydrocarbon-based organic solvent as the major components and having an adjusted water content, thereby subjecting the 1,3-butadiene to cis-1,4-polymerization and subsequently, (2) a step of making a catalyst obtainable from a soluble cobalt compound, an organoaluminum compound represented by the general formula,  $AlR_3$  (wherein R represents an alkyl group having from 1 to 6 carbon atoms, a phenyl group, or a cycloalkyl group), and carbon disulfide present in the resulting polymerization reaction mixture, thereby subjecting the 1,3-butadiene to 1,2-polymerization; and (B) a cis-polybutadiene solution obtained by a step of dissolving cis-polybutadiene containing 80 % or more of a cis-1,4-bond and having a Mooney viscosity ( $ML_{1+4}$  at 100 °C) of from 20 to 80 in a mixture containing 1,3-butadiene and/or a hydrocarbon-based organic solvent as the major component.
3. A process for producing a vinyl-cis-polybutadiene rubber, which comprises mixing (A) a vinyl-cis-polybutadiene solution obtained by (1) a step of dissolving cis-polybutadiene containing 80 % or more of a cis-1,4-bond and having a Mooney viscosity ( $ML_{1+4}$  at 100 °C) of from 20 to 80 in a mixture containing 1,3-butadiene and a

hydrocarbon-based organic solvent as the major components and subsequently, (2) a step of making a catalyst obtainable from a soluble cobalt compound, an organoaluminum compound represented by the general formula,  $AlR_3$  (wherein R represents an alkyl group having from 1 to 6 carbon atoms, a phenyl group, or a cycloalkyl group), and carbon disulfide present in the resulting cis-polybutadiene solution, thereby subjecting the 1,3-butadiene to 1,2-polymerization; and (B) cis-polybutadiene obtained by a step of adding said cis-1,4-polymerization catalyst, thereby subjecting the 1,3-butadiene to cis-1,4-polymerization.

4. A process for producing a vinyl-cis-polybutadiene rubber, which comprises mixing (A) a vinyl-cis-polybutadiene solution obtained by (1) a step of dissolving cis-polybutadiene containing 80 % or more of a cis-1,4-bond and having a Mooney viscosity ( $ML_{1+4}$  at 100 °C) of from 20 to 80 in a mixture containing 1,3-butadiene and a hydrocarbon-based organic solvent as the major components and having an adjusted water content and subsequently, (2) a step of making a catalyst obtainable from a soluble cobalt compound, an organoaluminum compound represented by the general formula,  $AlR_3$  (wherein R represents an alkyl group having from 1 to 6 carbon atoms, a phenyl group, or a cycloalkyl group), and carbon disulfide present in the resulting cis-polybutadiene solution, thereby subjecting the 1,3-butadiene to 1,2-polymerization; and (B) cis-polybutadiene obtained by a step of adding said cis-1,4-polymerization catalyst, thereby subjecting the 1,3-butadiene to cis-1,4-polymerization.

5. A process for producing a vinyl-cis-polybutadiene rubber, which comprises mixing (A) a vinyl-cis-polybutadiene solution obtained by (1) a step of dissolving cis-polybutadiene containing 80 % or more of a cis-1,4-bond and having a Mooney viscosity ( $ML_{1+4}$  at 100 °C) of from 20 to 80 in a mixture containing 1,3-butadiene and a hydrocarbon-based organic solvent as the major components and subsequently, (2) a step of making a catalyst obtainable from a soluble cobalt compound, an organoaluminum compound represented by the general formula,  $AlR_3$  (wherein R represents an alkyl group having from 1 to 6 carbon atoms, a phenyl group, or a cycloalkyl group), and carbon disulfide present in the resulting cis-polybutadiene solution, thereby subjecting the 1,3-butadiene to 1,2-polymerization; and (B) a cis-polybutadiene solution obtained by a step of dissolving cis-polybutadiene containing 80 % or more of a cis-1,4-bond and having a

Mooney viscosity (ML<sub>1+4</sub> at 100 °C) of from 20 to 80 in a mixture containing 1,3-butadiene and/or a hydrocarbon-based organic solvent as the major component.

6. A process for producing a vinyl-cis-polybutadiene rubber, which comprises mixing (A) a vinyl-cis-polybutadiene solution obtained by (1) dissolving cis-polybutadiene containing 80 % or more of a cis-1,4-bond and having a Mooney viscosity (ML<sub>1+4</sub> at 100 °C) of from 20 to 80 in a mixture containing 1,3-butadiene and a hydrocarbon-based organic solvent as the major components and having an adjusted water content and subsequently, (2) a step of making a catalyst obtainable from a soluble cobalt compound, an organoaluminum compound represented by the general formula, AlR<sub>3</sub> (wherein R represents an alkyl group having from 1 to 6 carbon atoms, a phenyl group, or a cycloalkyl group), and carbon disulfide present in the resulting cis-polybutadiene solution, thereby subjecting the 1,3-butadiene to 1,2-polymerization; and (B) a cis-polybutadiene solution obtained by a step of dissolving cis-polybutadiene containing 80 % or more of a cis-1,4-bond and having a Mooney viscosity (ML<sub>1+4</sub> at 100 °C) of from 20 to 80 in a mixture containing 1,3-butadiene and/or a hydrocarbon-based organic solvent as the major component.

7. The process for producing a vinyl-cis-polybutadiene rubber according to ~~any one of claims 1 to 6, claim 1,~~ wherein the polymerization temperature for a step of subjecting the 1,3-butadiene to 1,2-polymerization in said (A) (2) is from -5 to 50 °C.

8. The process for producing a vinyl-cis-polybutadiene rubber according to ~~any one of claims 1 to 7, claim 1,~~ wherein a proportion (HI) of a boiling n-hexane insoluble matter of the vinyl-cis-polybutadiene obtained in said (A) is from 10 to 60 % by weight.

9. The process for producing a vinyl-cis-polybutadiene rubber according to claim 1, wherein a viscosity in a 5 % toluene solution (T<sub>cp</sub>) of the cis-polybutadiene obtained in a step of subjecting to cis-1,4-polymerization in said (A) (1) is from 150 to 250.

10. The process for producing a vinyl-cis-polybutadiene rubber according to claim 2, wherein the cis-polybutadiene in said (B) is used as a single kind or a blend of two or more kinds of cis-polybutadiene synthesized by using a cobalt catalyst or a nickel catalyst or a lanthanoid catalyst.

11. The process for producing a vinyl-cis-polybutadiene rubber according to ~~claim 3 or 4, 3,~~ wherein the cis-polybutadiene in said (A) is used as a single kind or a

blend of two or more kinds of cis-polybutadiene synthesized by using a cobalt catalyst or a nickel catalyst or a lanthanoid catalyst.

12. The process for producing a vinyl-cis-polybutadiene rubber according to claim 5 or 6, 5, wherein the cis-polybutadiene in said (A) and (B) is used as a single kind or a blend of two or more kinds of cis-polybutadiene synthesized by using a cobalt catalyst or a nickel catalyst or a lanthanoid catalyst.

13. The process for producing a vinyl-cis-polybutadiene rubber according to claim 2, including a step of dissolving at least one member of previously polymerized polyisoprene, liquid polyisoprene, crystalline polybutadiene having a melting point of not higher than 150 °C, liquid polybutadiene, a styrene-indene-styrene compound, and derivatives thereof in a mixture containing 1,3-butadiene and a hydrocarbon-based solvent as the major components prior to the cis-1,4-polymerization or 1,2-polymerization in said (A) (1).

14. The process for producing a vinyl-cis-polybutadiene rubber according to any one of claims 3 to 6, claim 3, including a step of dissolving at least one member of previously polymerized polyisoprene, liquid polyisoprene, crystalline polybutadiene having a melting point of not higher than 150 °C, liquid polybutadiene, a styrene-indene-styrene compound, and derivatives thereof in a mixture containing 1,3-butadiene and a hydrocarbon-based solvent as the major components prior to initiation of the 1,2-polymerization in said (A) (1).

15. A rubber composition comprising 100 parts by weight of a rubber component containing the vinyl-cis-polybutadiene rubber according to any one of claims 1 to 14, claim 1, having from 10 to 100 parts by weight of a rubber reinforcing agent compounded therein.

16. A rubber composition for sidewall comprising 100 parts by weight of a rubber component made of (a) from 20 to 80 % by weight of a vinyl-cis-polybutadiene rubber resulting from solution mixing (A) vinyl-cis-polybutadiene obtained by (1) a step of adding a cis-1,4-polymerization catalyst obtainable from an organoaluminum compound and a soluble cobalt compound to a mixture containing 1,3-butadiene and a hydrocarbon-based organic solvent as the major components and having an adjusted water content, thereby subjecting the 1,3-butadiene to cis-1,4-polymerization and subsequently, (2) a step of making a catalyst obtainable from a soluble cobalt compound, an organoaluminum compound represented by the general formula,  $AlR_3$  (wherein R represents an alkyl group having from 1 to 6 carbon atoms,

a phenyl group, or a cycloalkyl group), and carbon disulfide present in the resulting polymerization reaction mixture, thereby subjecting the 1,3-butadiene to 1,2-polymerization and (B) cis-polybutadiene obtained by a step of adding said cis-1,4-polymerization catalyst, thereby subjecting the 1,3-butadiene to cis-1,4-polymerization, and (b) from 80 to 20 % by weight of a diene-based rubber other than (a); and (c) from 25 to 60 parts by weight of a rubber reinforcing agent.

17. A silica compounded rubber composition for tire comprising 100 parts by weight of a rubber component made of (a) from 20 to 80 % by weight of a vinyl-cis-polybutadiene rubber resulting from solution mixing (A) vinyl-cis-polybutadiene obtained by (1) a step of adding a cis-1,4-polymerization catalyst obtainable from an organoaluminum compound and a soluble cobalt compound to a mixture containing 1,3-butadiene and a hydrocarbon-based organic solvent as the major components and having an adjusted water content, thereby subjecting the 1,3-butadiene to cis-1,4-polymerization and subsequently, (2) a step of making a catalyst obtainable from a soluble cobalt compound, an organoaluminum compound represented by the general formula,  $AlR_3$  (wherein R represents an alkyl group having from 1 to 6 carbon atoms, a phenyl group, or a cycloalkyl group), and carbon disulfide present in the resulting polymerization reaction mixture, thereby subjecting the 1,3-butadiene to 1,2-polymerization and (B) cis-polybutadiene obtained by a step of adding said cis-1,4-polymerization catalyst, thereby subjecting the 1,3-butadiene to cis-1,4-polymerization, and (b) from 80 to 20 % by weight of a diene-based rubber other than (a); and (c) from 40 to 100 parts by weight of a rubber reinforcing agent containing 40 % or more of silica.

18. A rubber composition for passenger automobile tire comprising 100 parts by weight of a rubber component made of (a) from 10 to 50 % by weight of a vinyl-cis-polybutadiene rubber resulting from solution mixing (A) vinyl-cis-polybutadiene obtained by (1) a step of adding a cis-1,4-polymerization catalyst obtainable from an organoaluminum compound and a soluble cobalt compound to a mixture containing 1,3-butadiene and a hydrocarbon-based organic solvent as the major components and having an adjusted water content, thereby subjecting the 1,3-butadiene to cis-1,4-polymerization and subsequently, (2) a step of making a catalyst obtainable from a soluble cobalt compound, an organoaluminum compound represented by the general formula,  $AlR_3$  (wherein R represents an alkyl group having from 1 to 6 carbon atoms, a phenyl group, or a

cycloalkyl group), and carbon disulfide present in the resulting polymerization reaction mixture, thereby subjecting the 1,3-butadiene to 1,2-polymerization and (B) cis-polybutadiene obtained by a step of adding said cis-1,4-polymerization catalyst, thereby subjecting the 1,3-butadiene to cis-1,4-polymerization, (d) from 30 to 70 % by weight of a styrene-butadiene rubber, and (b) from 0 to 60 % by weight of a diene-based rubber other than (a) and (d); and (c) from 40 to 100 parts by weight of a rubber reinforcing agent.

19. A rubber composition for tire cord coating comprising 100 parts by weight of a rubber component made of (a) from 10 to 60 % by weight of a vinyl-cis-polybutadiene rubber resulting from solution mixing (A) vinyl-cis-polybutadiene obtained by (1) a step of adding a cis-1,4-polymerization catalyst obtainable from an organoaluminum compound and a soluble cobalt compound to a mixture containing 1,3-butadiene and a hydrocarbon-based organic solvent as the major components and having an adjusted water content, thereby subjecting the 1,3-butadiene to cis-1,4-polymerization and subsequently, (2) a step of making a catalyst obtainable from a soluble cobalt compound, an organoaluminum compound represented by the general formula,  $AlR_3$  (wherein R represents an alkyl group having from 1 to 6 carbon atoms, a phenyl group, or a cycloalkyl group), and carbon disulfide present in the resulting polymerization reaction mixture, thereby subjecting the 1,3-butadiene to 1,2-polymerization and (B) cis-polybutadiene obtained by a step of adding said cis-1,4-polymerization catalyst, thereby subjecting the 1,3-butadiene to cis-1,4-polymerization, and (b) from 90 to 40 % by weight of a diene-based rubber other than (a); and (c) from 30 to 80 parts by weight of a rubber reinforcing agent.

20. A rubber composition for base tread comprising 100 parts by weight of a rubber component made of (a) from 20 to 80 % by weight of a vinyl-cis-polybutadiene rubber resulting from solution mixing (A) vinyl-cis-polybutadiene obtained by (1) a step of adding a cis-1,4-polymerization catalyst obtainable from an organoaluminum compound and a soluble cobalt compound to a mixture containing 1,3-butadiene and a hydrocarbon-based organic solvent as the major components and having an adjusted water content, thereby subjecting the 1,3-butadiene to cis-1,4-polymerization and subsequently, (2) a step of making a catalyst obtainable from a soluble cobalt compound, an organoaluminum compound represented by the general formula,  $AlR_3$  (wherein R represents an alkyl group having from 1 to 6 carbon atoms, a phenyl group, or a cycloalkyl group), and

carbon disulfide present in the resulting polymerization reaction mixture, thereby subjecting the 1,3-butadiene to 1,2-polymerization and (B) cis-polybutadiene obtained by a step of adding said cis-1,4-polymerization catalyst, thereby subjecting the 1,3-butadiene to cis-1,4-polymerization, and (b) from 80 to 20 % by weight of a diene-based rubber other than (a); and (c) from 22 to 55 parts by weight of a rubber reinforcing agent.

21. A high-hardness compounded rubber composition comprising 100 parts by weight of a rubber component made of (a) from 20 to 80 % by weight of a vinyl-cis-polybutadiene rubber resulting from solution mixing (A) vinyl-cis-polybutadiene obtained by (1) a step of adding a cis-1,4-polymerization catalyst obtainable from an organoaluminum compound and a soluble cobalt compound to a mixture containing 1,3-butadiene and a hydrocarbon-based organic solvent as the major components and having an adjusted water content, thereby subjecting the 1,3-butadiene to cis-1,4-polymerization and subsequently, (2) a step of making a catalyst obtainable from a soluble cobalt compound, an organoaluminum compound represented by the general formula,  $AlR_3$  (wherein R represents an alkyl group having from 1 to 6 carbon atoms, a phenyl group, or a cycloalkyl group), and carbon disulfide present in the resulting polymerization reaction mixture, thereby subjecting the 1,3-butadiene to 1,2-polymerization and (B) cis-polybutadiene obtained by a step of adding said cis-1,4-polymerization catalyst, thereby subjecting the 1,3-butadiene to cis-1,4-polymerization, and (b) from 80 to 20 % by weight of a diene-based rubber other than (a); and (c) from 60 to 100 parts by weight of a rubber reinforcing agent.

22. A rubber composition for large-sized vehicle tire comprising 100 parts by weight of a rubber component made of (a) from 10 to 60 % by weight of a vinyl-cis-polybutadiene rubber resulting from solution mixing (A) vinyl-cis-polybutadiene obtained by (1) a step of adding a cis-1,4-polymerization catalyst obtainable from an organoaluminum compound and a soluble cobalt compound to a mixture containing 1,3-butadiene and a hydrocarbon-based organic solvent as the major components and having an adjusted water content, thereby subjecting the 1,3-butadiene to cis-1,4-polymerization and subsequently, (2) a step of making a catalyst obtainable from a soluble cobalt compound, an organoaluminum compound represented by the general formula,  $AlR_3$  (wherein R represents an alkyl group having from 1 to 6 carbon atoms, a phenyl group, or a cycloalkyl group), and carbon disulfide present in the

resulting polymerization reaction mixture, thereby subjecting the 1,3-butadiene to 1,2-polymerization and (B) cis-polybutadiene obtained by a step of adding said cis-1,4-polymerization catalyst, thereby subjecting the 1,3-butadiene to cis-1,4-polymerization, and (b) from 90 to 40 % by weight of a diene-based rubber other than (a); and (c) from 45 to 70 parts by weight of a rubber reinforcing agent.

23. The rubber composition according to ~~any one of claims 16 to 22, claim 16~~, wherein in the production step of the vinyl-cis-polybutadiene rubber (a), the polymerization temperature for a step of subjecting the 1,3-butadiene to 1,2-polymerization in said (A)(2) is from -5 to 50 °C.

24. The rubber composition according to ~~any one of claims 16 to 22, claim 16~~, wherein in the production step of the vinyl-cis-polybutadiene rubber (a), a proportion (HI) of a boiling n-hexane insoluble matter of the vinyl-cis-polybutadiene obtained in said (A) is from 10 to 60 % by weight.

25. The rubber composition according to ~~any one of claims 16 to 22, claim 16~~, wherein in the vinyl-cis-polybutadiene rubber (a), a viscosity in a 5 % toluene solution (T<sub>cp</sub>) of the cis-polybutadiene obtained in a step of subjecting to cis-1,4-polymerization in said (A)(1) is from 150 to 250.

26. The rubber composition according to ~~any one of claim 16, 18, 19, 20, 21 or 22~~, wherein the diene-based rubber (b) other than (a) is a natural rubber and/or polyisoprene.

27. The rubber composition according to claim 17, wherein the diene-based rubber (b) other than (a) is a natural rubber and/or polyisoprene and/or a styrene-butadiene rubber.

28. The rubber composition according to ~~any one of claims 16 to 22, claim 16~~, wherein the rubber reinforcing agent (c) is carbon black.